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National Aeronautics and Space Administration
Houston 1, Texas

Contract No. NASr-70

## ELECTROLYTIC PRODUCTION OF OXYGEN AND REDUCTION OF CARBON DIOXIDE

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4 June 1963

# MSA Research Corporation

*Subsidiary of Mine Safety Appliances Company*

## Callery, Pennsylvania

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ABSTRACT

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Work is reported on studies of the cathodic reduction of carbon dioxide with simultaneous anodic production of breathing oxygen from aqueous solutions.

Studies included those of analytical procedures for possible organic products such as formic acid, formaldehyde, methanol and methane. Details are given on the chemical and gas chromatographic procedures adopted for routine analysis.

Details of studies of various parameters normally influencing cathodic reduction are given. It was found that use of mercury cathodes and electrolytes of either $Li_2SO_4$, $K_2SO_4$, $Na_2SO_4$ or $BeSO_4$ consistently gave rise to reduction of $CO_2$ to formic acid with efficiencies as high as 20%. However, while concentrated formic acid was reduced, further reduction of the formic acid of the concentrations up to 1% obtained by reduction of $CO_2$ was not obtained. Since such further reduction is needed for good control of space capsule atmospheres, no attempt was made to develop a prototype system for atmosphere control.

AUTHOR

Final Report

to

National Aeronautics and Space Administration
Houston 1, Texas

on

ELECTROLYTIC PRODUCTION OF OXYGEN AND REDUCTION OF CARBON DIOXIDE

I.  INTRODUCTION

The work performed under the subject contract involved the
investigation of scientific principles and processes for the anodic
production of breathing oxygen and the simultaneous cathodic re-
duction of carbon dioxide.  A number of variables influence these
processes, including cathode current density, cathode material and
physical structure, types of diaphragms, electrolyte composition,
temperature, pressure; and these variables were studied along with
methods of analysis for the various possible products of reduction.
Details of these studies were reported in Status Reports I through
VI on the subject contract and a paper prepared for publication in
Proceedings of the Symposium on Space Vehicle Thermal and Atmosphere
Control (1963).  The overall result of these studies was the  es-
tablishment of sensitive and accurate methods of analysis and the
demonstration of reduction of carbon dioxide to formic acid and
of higher concentrations of formic acid to trace amounts of formal-
dehyde.

This final report is presented to summarize the results re-
ported in the Status Reports, to collate these results and those
reported in the literature and to make assessment of the proposed
processes and of related but unstudied processes.

## II. CONCEPT

Cathodic reduction of reducible compounds is a standard electrochemical process. It was conceived that reduction of carbon dioxide to formic acid, formaldehyde or methanol might be coupled with anodic production of oxygen in an aqueous system as a means of control of atmospheres in confined spaces. If reducibility to equimolar amounts of formaldehyde and methanol could be demonstrated, complete consumption of carbon dioxide and full production of human breathing oxygen would be attainable. This is based on the fact that production of carbon dioxide represents utilization of 82% of the human's oxygen requirement. If oxygen were produced from carbon dioxide mole per mole, then 82% of the oxygen requirement would be produced. This process would be obtained in production of formaldehyde according to the equation:

$$(1) \quad CO_2 + H_2O \longrightarrow HCHO + O_2$$
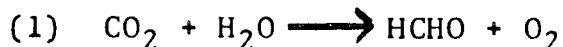
Production of 123% of the human oxygen requirement would be obtained from production of methanol according to the equation:

$$(2) \quad CO_2 + 2H_2O \longrightarrow CH_3OH + 3/2O_2$$

The sum of equations 1 and 2 would then be

$$(3) \quad 2CO_2 + 3H_2O \longrightarrow HCHO + CH_3OH + 5/2O_2$$

Thus, cathodic reduction of carbon dioxide to equimolar amounts of formaldehyde and methanol would be an interesting tool for atmosphere control, resulting in production of breathing oxygen and in conversion of carbon dioxide to liquid products with consumption of water, which could be obtained from recycled urine or from condensate of cabin air. An intriguing extension is the use of the formaldehyde and methanol to produce edible materials by synthesis.

## III.  ANALYTICAL DEVELOPMENTS

An investigation of analytical methods for anticipated pro-
ducts was carried out concurrently with the electrolysis experi-
ments.  These anticipated products from the reduction of $CO_2$
included aqueous solutions containing formaldehyde, formic acid,
methanol, methylal and possibly methyl formate; and gaseous pro-
ducts such as methane, carbon dioxide, hydrogen, oxygen and carbon
dioxide.  As work progressed experiments were conducted with or-
ganic solvents and it became necessary to analyse for the elec-
trolysis products in the presence of various organic solvents.

The analytical methods used to monitor the experimental cells
were selected in order to fulfill two basic requirements: the need
for rapid qualitative tests in order to follow closely the course
of the experiments, and quantitative methods for final evaluation.

Gas chromatography was adopted as the most versatile ana-
lytical method.  A testing program of various column packings was
carried out in order to find a system for the analysis of aqueous
solutions of the expected organics.  A satisfactory column was
found that adequately resolved methyl formate, methanol, methylal,
water and formaldehyde but was not effective for formic acid.  The
column also resolved various organic solvents such as dioxane,
acetone, ethers and pyridine which allowed analysis of the organic
electrolyte systems.  Chemical methods for formic acid were found
necessary.

Gas chromatography was also used for analysis of the gas phase
containing carbon monoxide, methane, hydrogen and oxygen.  Carbon
dioxide was analyzed, when necessary, on a mass spectrometer.

## Analysis of Electrolytes

A sample up to 10 ml was taken from the cathode or anode of
the electrolysis cell.  A qualitative test for formaldehyde was
made using a modified Schiff's Reagent.[23]  To 5 ml of sample cooled
in an ice bath containing 10-50 ug of formaldehyde, 1 ml of con-
centrated $H_2SO_4$ was added.  After allowing to cool, 5 ml of Schiff
Reagent (Fisher Scientific Co.) was added and the solution removed
from the ice bath.  A blue color develops after standing, indi-
cating a positive test for formaldehyde.  A quantitative result
up to 15 ug could be attained by reading the absorption on a
photometer at 570 to 590 mu.

A qualitative test for formic acid was also run on the sample.
In the absence of formaldehyde, formic acid was reduced to formal-
dehyde with magnesium in acid solution and tested for formaldehyde
with the Schiff Reagent.  To one ml of sample immersed in an ice

bath was added a small coil of magnesium ($\sim$80 mg). Concentrated $H_2SO_4$ was added dropwise at the rate of 1 drop per minute until the magnesium was completely reacted. The solution was tested for formaldehyde by adding 1 ml of concentrated $H_2SO_4$ and 5 ml of the Schiff Reagent. A positive formic acid was indicated by a blue color. If formaldehyde is present in the original sample, it can be removed by adding a small amount of phenylhydrazine hydro-chloride before reduction with magnesium. Methanol does not interfere with the method.

After the preliminary qualitative tests for formaldehyde and formic acid, the remaining sample required distillation in order to separate the inorganic salts before injection into the chromato-graph. The sample was made acid with $H_2SO_4$ and distilled. A 2 ul sample was then injected into the chromatograph for the quantitative analysis of formaldehyde, methanol or other volatile organics present.

A Wilkens Instrument and Research, Inc. A-90-P chromatograph was used for the analysis with a 15 ft long 1/4 inch diameter copper column packed with 10% Ethofat 60/25 (Armour Industrial Co.) on 40-60 mesh Columpak-T (Fisher Scientific Co.). The helium carrier gas flowrate was 40 cc/min, column temperature 120°C, sample in-jection temperature 150°C and a sample size of 2 ul. The column adequately resolved the following compounds: methyl formate, acetone, ethers, methyl alcohol, methalyl, pentanone, pyridine, acetonitrile, water and formaldehyde. Individual calibrations for methanol and formaldehyde were made by injecting known amounts and measuring peak area. A stock solution of formaldehyde was prepared by refluxing para-formaldehyde in water for two hours and filtering. The for-maldehyde concentration of this stock solution was determined by the sodium sulfite method.[24] Standards were prepared by appropriate dilutions with water. Aqueous formaldehyde and methanol were de-termined in concentrations as low as 0.1%.

Quantitative analysis of formic acid was performed on the electrolytes at the end of the run by the alkaline oxidation of the formate with standard $KMnO_4$. An aliquot of the solution to be analyzed was made acid with $H_2SO_4$ and distilled into a $Na_2CO_3$ solution. The distillate was warmed slightly and an excess of N/10 $KMnO_4$ was added. $MnO_2$ precipitated as the formate was oxidized. A quantity of 10 ml of dilute $H_2SO_4$ was added and an excess of N/10 oxalic acid was added until all the precipitate dissolved. The excess oxalic acid was titrated with N/10 permanganate and the formic acid content determined by the $KMnO_4$ required.

## Analysis of Gas Phases

Where applicable, gases were collected in a 200 ml gas buret and transferred to the chromatograph by a gas-tight syringe or passed directly through the instrument's sampling valve.

A Consolidated Electrodynamics Model 26-201 gas chromatograph equipped with a 6 ft long 1/4 inch diameter copper column packed with 13X Molecular Sieves was used for the routine analysis of hydrogen, oxygen, methane and carbon monoxide. Helium flowrate was 80 cc/min at a column temperature of 30°C. Calibrations were made by using known mixtures and measuring the peak height. Methane was detected as low as 50 ppm and CO to 100 ppm using a 1 mv recorder.

A Consolidated Electrodynamics 21-620 mass spectrometer was used for analysis of $CO_2$ or for confirming analysis where necessary.

## Results of Analytical Procedures

Elution times of various compounds of interest are shown in Table 1. These compounds include both possible products and solvents and both liquid and gas phases. The elution times are from columns operated according to the detailed procedures above.

## TABLE 1 - ELUTION TIMES OF VARIOUS COMPOUNDS

| Liquid Phase Compound | Time (Min) | Gas Phase Compound | Time (Min) |
|---|---|---|---|
| Air | 1.6 | Hydrogen | 0.6 |
| Ether | 2.7 | Oxygen | 1.1 |
| Methyl formate | 2.9 | Nitrogen | 1.8 |
| Methylal | 3.3 | Methane | 3.1 |
| Acetone | 3.8 | Carbon monoxide | 4.7 |
| Methanol | 4.6 | | |
| Water | 5.9 | | |
| Acetonitrile | 6.2 | | |
| Pentanone | 8.3 | | |
| Dioxane | 12.3 | | |
| Formaldehyde | 14 | | |
| Pyridine | 20 | | |

## IV. ELECTROCHEMICAL STUDIES

As was mentioned in the Introduction above, variables such as current density, electrode material and physical structure, type of diaphragm, catalyst, electrolyte composition, promoters, temperature and pressure influence electrode reactions and products thereof. These variables, therefore, were the subject of experimental study, on reduction of both $CO_2$ and formic acid. Details are reported in the various Status Reports on the subject contract and are summarized in Table 2. To simplify tabulation in Table 2, runs 73 through 79 are not listed. These runs involved studies of direct reduction of $CO_2$ and aqueous formic acid with alkali and alkaline earths and their amalgams. Results showed $CO_2$ to be reduced to formic acid by potassium amalgam and small amounts of formic acid to formaldehyde by lithium, calcium and beryllium but not by amalgams of potassium, lithium, calcium, sodium or magnesium. Similarly, runs 132-135 and 158-179 are not tabulated for reasons of conciseness since they all involved use of organic catholyte solvents and showed either extremely low conductivities with no detectable current at 45 volts or showed no detectable reductions. They included systems with solvents of ether, dioxane, bis-2-dimethoxyethyl ether, acetone, anisole, pentanone, pyridine, acetonitrile, propylene carbonate, both with and without Raney nickel catalyst and both with cation exchange membranes between organic catholyte and aqueous anolyte and without membranes. It was hoped that reduction of $CO_2$ might be obtained without reduction of the solvent. However, when some reduction products were detected, it was found in blank runs that these products were the result of decomposition of the organic solvents. Systems with poor conductivity are listed in Table 3 and those with no detectable reduction in Table 4. Platinum anodes were used throughout all the tests.

During this investigation the cells used ranged from a simple "beaker" type cell to a one liter autoclave at 50 atmospheres $CO_2$. Under these circumstances each cell was set up and operated according to the experimental objective. However, the following general procedure was used for all cells: The electrolytes were made up according to the experimental conditions and placed in the prepared cell. Pressure cells were tested for leaks before electrolysis was started. The current was adjusted to the desired level and the cell was thermostatted as required. Most runs were of long duration therefore it was necessary to adjust the current at regular intervals. Samples were extracted from the cell and analyzed for the products of interest at intervals during the electrolysis.

TABLE 2 - SUMMARY OF ELECTROCHEMICAL TESTS

| Run | Type of Cell | Diaphragm | Anolyte | Cathode | Catholyte | Time (hrs) |
|---|---|---|---|---|---|---|
| 1 | U tube of 2" pipe rubbercoated | 1 7/8 x 5" aluminum cup | Sat. $Li_2SO_4$ sol. | Folded in Zn sheet | Sat. $Li_2SO_4$ sol. | 3 up to 150 lbs |
| 2 | " | " | " | " | " | 3 up to 300 lbs |
| 3 | Glass H cell | Small ceramic cup | Sat. $Li_2SO_4$ sol. | 10" x 5" Zn sheet folded | Sat. $Li_2SO_4$ 10% HCOOH | 4 |
|  | " |  |  |  |  | 16 |
| 4 | Glass H cell | " | " | Zn rod | " | 3 |
| 5 | " |  |  |  |  | 16 |
| 6 | Concentric | 1 3/4" x 6" Norton alundum cup | " | Amalgamated Zn sheet folded | " | 6 |
| 7 | Concentric |  |  | Zn rod | " | 6 |
| 8 | Concentric | " | " | Amalgamated Zn sheet folded | " | 7 |
| 9 | Concentric | New   " | Fresh " | New Zn rod | Fresh " | 7 |
| 10 | Continued |  |  |  |  | 16 |
| 11 | Continued |  |  |  | $H_2SO_4$ added | 6 |
| 12 | Glass H cell | Small alundum cup with double layer cellophane | Sat. $Li_2SO_4$ sol. | New Zn rod | Sat. $Li_2SO_4$ 10% HCOOH | 5 |
| 13 | Glass H cell | New cup and double layer cellophane | " | Zn sheet folded | " | 5 |
| 14 | Continued |  |  |  |  | 16 |
| 15 | Glass H cell | " | " | New Zn rod | Sat. $Li_2SO_4$ 10% HCOOH | 4 |
| 16 | Continued |  |  |  |  | 16 4 2 |
| 17 | New H cell | 1 3/4" x 6" alundum cup | 30% $LiClO_4$ sol. | Folded Zn sheet | 30% $LiClO_4$ 10% HCOOH | 3 2 |
| 18 | New H cell | " | 15 ml $H_2SO_4$ added |  |  | 6 |
| 19 | U tube of 2" pipe rubber coated | 1 3/4" x 6" alundum cup | Sat. $Li_2SO_4$ sol. | New folded Zn sheet | Sat. $Li_2SO_4$ sol. | 3 300 lbs |
|  | continued |  |  |  |  | 7 300 lbs |
| 20 | " |  | 30 ml $H_2SO_4$ added |  |  | 6 200 lbs 20 hrs |
| 21 | Glass U tube | Conc. $H_2SO_4$ bottom of U | Sat. $Li_2SO_4$ sol. | Amalgamated Zn sheet | LiCl Sol. HCOOH added | 3 |
| 22 | Glass H cell | Alundum cup | $Li_2SO_4$ sol. | New Zn rod | $Li_2SO_4$ HCOOH | 18 |
| 23 | Glass H cell | Alundum cup | New   " | Zn rod from above | New   " | 20 |
| 24 | Glass H cell | " | " | " | " | 18 |
| 25 | Glass H cell | " | " | " | " | 20 |
| 26 | Glass U tube | Alundum cup | $Li_2SO_4$ sol. | New Zn sheet | $Li_2SO_4$ HCOOH | 18 |
|  | continued |  |  |  |  | 25 |
| 27 | Large H cell | Large alundum cup | $Li_2SO_4$ sol. | 3 new Zn rods | $Li_2SO_4$ HCOOH | 18 |
| 28 | Continued |  |  |  |  | 7 |
| 29 | Above cell washed and refilled | " | " | New Zn sheet | " | 16 |

| Amps | Cathode Current Density $(ma/cm^2)$ | Volts | Tests | Remarks |
|------|------|------|------|------|
| 2.5 - 3 | 3.86 - 4.66 | 14 - 8 | Schiffs positive for HCHO, basic. Heavy precipitate. | Later same sample, may test for both HCHO and HCOOH. Cell became quite warm. |
| " | " | " | Anode gas-$O_2$, no HCHO cathode - 30% $CO_2$ | Black insulating film on Zn. |
| 0.3 | .465 | 13 | Trace HCHO | Grey ppt formed. Conductivity increased. |
| high | | 10 | No HCHO. Basic, formate present. | Much ppt. Much Zn deposit next leg, corrosion opposite. |
| 0.3 | 13.3 | 13 | No HCHO | |
| 0.3 | " | 13 | No HCHO | Once an immediate violet which soon faded. Considerable Zn deposit. |
| 3.5 - 4 | 5.4 - 6.2 | 5 | No HCHO | Cell became warm. Hg-Zn electrode remained shiny. |
| 3 - 4 | 4.6 - 6.2 | 5 | No HCHO | Zn developed black film. No organics in cathode gas by IR. |
| 1 | 1.5 | 3.5 | No HCHO | Significant $CO_2$ in anode gas by IR. |
| 0.2 | 8.9 | 2.5 | No HCHO | |
| | | | No HCHO | |
| | | | No HCHO | |
| 0.2 | 8.9 | 3 | No HCHO | Tests showed the formate came through the cellophane readily. |
| 0.2 - 0.3 | 0.31 - .46 | 12 - 14 | No HCHO | |
| high | | | No HCHO, basic | Water level down, cell hot, much grey ppt both sides. |
| .03 | 1.3 | 5 | No HCHO | |
| | | | Trace HCHO More HCHO Less HCHO | |
| .3 | 0.46 | 5 | No HCHO | Trace $Cl_2$ from anode by Draeger tubes. |
| .15 | 0.23 | 4 | No HCHO | " |
| .2 | 0.31 | 4 | No HCHO | |
| .3 | 0.46 | 5.5 | No HCHO or HCOOH Heavy precipitate. | Over 90% $O_2$ from anode as press lowered. Nearly 100 $CO_2$ from cathode as press lowered. |
| .45 | 0.70 | 5.7 | No HCHO, basic Heavy precipitate. | Precipitate dissolves with acid, evolving gas. |
| .4 | 0.62 | 5 | " | Precipitate dissolves. Electrolyte clear green. |
| .05 | 0.08 | 12 | AgNO3 indicated Cl in anolyte. No HCHO. | Reaction at LiCl - $H_2SO_4$ interface. |
| .05 | 2.2 | 5 | Good HCHO | |
| .05 | " | 5.2 | Faint HCHO test. | |
| .05 | " | 5.2 | No HCHO | |
| .05 | " | 5.2 | Faint HCHO test | Still much HCOOH in catholyte. |
| .01 | 0.016 | 5 | Good HCHO test | |
| | | | Good HCHO test | |
| .05 | 0.75 | 3.3 | Faint HCHO test | |
| .14 | 2.1 | 5 | Good HCHO test | |
| .13 | 0.2 | 5 | Faint HCHO test | |

| Run | Type of Cell | Diaphragm | Anolyte | Cathode | Catholyte | Time (hrs) |
|---|---|---|---|---|---|---|
| 30 | Continued | | | | | 4 |
| 31 | Continued | " | " | " | " | 20 |
| 32 | Concentric | Around large alundum cup | " | New Zn sheet | " | 18 |
| 33 | Continued | | | | | 5 |
| 34 | Continued | | | | | 20 |
| 35 | Glass U tube | Alundum cup | 6.5% tetra-butyl-ammonium iodide in 75% dioxane | New Zn rod | Anolyte + HCOOH | 40 |
| 36 | Glass U tube | Alundum cup | $Li_2SO_4$ sol. | Zn sheet | $Li_2SO_4$ HCOOH | 20 |
| 37 | Large H cell | Large alundum cup | " | " | " | 60 |
| 38 | Continued | " | " | Blackened section removed | " | 20 |
| 39 | Continued | " | " | " | " | 20 |
| 40 | Glass H cell | Alundum cup | " | Pt sheet | " | 20 |
| 41 | Continued | | | | | 20 |
| 42 | Continued | | | Amalgamated Zn sheet | " | |
| 43 | Continued | | | Zn rod used previously | | 20 |
| 44 | New U tube of 35 mm tubing | Parchment | $Li_2SO_4$ sol. | New Zn sheet | $Li_2SO_4$ HCOOH | 20 |
| 45 | 35 mm U cell | Alundum in cellophane | " | Zn sheet | " | 20 |
| 46 | 35 mm U cell | " | $Li_2SO_4$ sol. | Cd. rod | " | 20 20 |
| 47 | Concentric | Large alundum cup | " | Zn sheet outside cup | " | 60 |
| 48 | Small U tube | Dowex 50W-X8 | $H_2SO_4$ Sol. | Zn sheet | " | 30 |
| 49 | Large H cell | Alundum cup | $Li_2SO_4$ Sol. | Mg rod 5/8" dia. | $Li_2SO_4$ HCOOH HCOONa | 3 |
| 50 | Concentric | Large alundum cup | $Na_2SO_4$ Sol. | Mg rod | " | 1 |
| | Continued | | | | | 2 |
| 51 | Large H cell | " | " | " | $Na_2SO_4$ HCOONa $H_2SO_4$ added | 20 |
| | Continued | | | | | 20 |
| 52 | 35 mm U cell | Alundum in cellophane | $Li_2SO_4$ Sol. | Zn sheet | $Li_2SO_4$ HCOOH | 20 |
| 53 | Glass H cell | Alundum cup | $Na_2SO_4$ Sol. | 1/4" lead rod | 20% $Na_2SO_4$ 10% HCOOH | 6 |
| 54 | Glass H cell | | | | $Sb_2O_5$ added | 20 |
| 55 | Glass H cell | | | | $H_2SO_4$ added | 20 |
| 56 | Large U cell | Large alundum cup | $Na_2SO_4$ Sol. | 1/4" amalgamated Cu U tube | 20% $Na_2CO_4$ 10% HCOOH | 6 |
| 57 | Large U cell | " | " | " | $H_2SO_4$ added | 20 |
| 58 | Large H cell | Large alundum cup | $Li_2SO_4$ Sol. | Hg and dry ice | 10% $Li_2SO_4$ | 2 |
| 59 | Large H cell | " | " | Hg | " | 20 |
| 60 | Large H cell | Large alundum cup | 10% $Li_2SO_4$ 5% $H_2SO_4$ | Hg | 10% $Li_2SO_4$ 5% $H_2SO_4$ | 2 |
| 61 | " | " | " | " | " | 5 |

| Amps | Cathode Current Density (ma/cm²) | Volts | Tests | Remarks |
|---|---|---|---|---|
| .25 | 0.39 | 7.5 | Fainter HCHO test | |
| .15 | 0.23 | 5 | Good HCHO | |
| .1 | 0.15 | 2.6 | No HCHO | |
| 1.0 | 1.5 | 3.7 | No HCHO | |
| .05 | 0.08 | 2.6 | No HCHO | |
| .003 | 0.13 | 25 | Catholyte lost yellow color. | Gave deep red with Schiffs. Yellow ppt with $H_2SO_4$. Free $I_2$ on anode. |
| .005 | 0.008 | 5 | Good HCHO | |
| .03 | 0.047 | 3 | Good HCHO | Only previously used section of Zn sheet was producing gas. It was badly corroded. |
| .12 | 0.186 | 5 | No increase in HCHO | |
| .12 | 0.186 | 5 | Good HCHO | |
| .05 | 1.4 | 5 | No HCHO | To determine if a hydrogenation catalyst instead of the overvoltage was responsible for HCHO formation. |
| " | " | " | " | " " " |
| " | 0.07 | " | " | " " " |
| " | 2.0 | " | Trace HCHO | |
| .05 | 0.07 | 3 | Very good HCHO | Nothing by gas chromatograph. HCHO appeared to go through parchment. |
| .1 | 0.15 | 4 | Some HCHO | Considerable plating of Zn. |
| .12 | 1.3 | 5 | No HCHO Trace HCHO | No corrosion or plating of Cd. |
| .15 | 0.97 | 3 | No HCHO | Zn not attacked much. |
| .05 | 0.07 | 6 | Good HCHO | Connecting leg filled with exchange resin. No HCHO or HCOOH diffused to anolyte. |
| .5 | 8.3 | 10 | Good HCHO | From action of acid on Mg. |
| 4.5 | 75 | 15 | | Overheated |
| 1.0 | 16.7 | 5 | Good HCHO | |
| .6 | 10 | 14 | No HCHO | Brown jelly-like ppt - dissolves in acid. |
| .7 | 11.7 | 10 | No HCHO | |
| .1 | 0.15 | 5 | Good HCHO | Zn chips in U. HCOOH added from anode side. Zn deposit non-adhering. |
| .5 | 22.2 | 20 | No HCHO | Cell in ice bath. |
| " | " | " | " | Catholyte became basic. |
| " | " | " | Trace | |
| 1 - 3 | 22.2 - 66.7 | 24 | No HCHO | Ice water through cathode. Cell in ice bath. |
| 1 | 22.2 | 20 | No HCHO | Most Hg lost from cathode. |
| 1 | 66 | 20 | Some formate - no HCHO. | Dry ice held under Hg as $CO_2$ source. |
| 1 | 66 | 20 | No HCHO | No $CO_2$ added. Attempt to reduce HCOOH from #58. |
| 2.5 | 165 | 19 | No formate | Dry ice under Hg as $CO_2$ source. |
| 1 | 66 | 18 | No formate or HCHO | Tank $CO_2$ bubbled through Hg. In ice bath. |

| Run | Type of Cell | Diaphragm | Anolyte | Cathode | Catholyte | Time (hrs) |
|-----|-------------|-----------|---------|---------|-----------|------------|
| 62 | " | " | " | " | " | 20 |
| 63 | Small H cell | Alundum cup | $K_2SO_4$-$H_2SO_4$ | K-Hg amalgam | $K_2SO_4$ | 4 |
| 64 | 35 mm U cell | Alundum cup | HCOOH-$H_2SO_4$ | 1/4" dia. x 1 1/2 lead rod | HCOOH 10% $H_2SO_4$ | 2 |
| 65 | " | " | " | " | $Ce(SO_4)_2$ added | 2 |
| 66 | " | " | " | " | " | 50 |
| 67 | " | " | $H_2O$ added | Porous Ni | " | 20 |
| 68 | " | " | " | Lead rod | " | 40 |
| 69 | Large H cell | Large alundum cup | $MgSO_4$ | Hg with Mg rod | $MgSO_4$ | 2 |
| 70 | " | " | " | " | HCOOH added | 1 |
| 71 | Small H cell | Alundum cup | $MgSO_4$ | Hg | $MgSO_4$ | 20 |
| 72 | " | | " | " | HCOOH added | 20 |
| 80 | 2" pyrex pipe | Cation exchange | 10% $MgSO_4$ | Mg 3/4" rod | $MgCO_3$ slurry | 16 |
| 81 | " | " | " | " | " | 7 |
| 82 | H cell | Alundum cup | Sat $BeSO_4$ + $H_2SO_4$ | Hg | HCOOH added | 18 |
| 83 | 35 mm U cell | Alundum cup | 10% $H_2SO_4$ | Speer graphite | 10% $H_2SO_4$ | 4 |
| 84 | H Cell | Alundum cup | Sat $BeSO_4$ | Hg | Sat $BeSO_4$ | 15+ |
| 85 | " | | | | " + HCOOH formed | 60 |
| 86 | U cell | " | $H_2SO_4$(10%) | Speer graphite | 10% HCOOH + 10% $H_2SO_4$ | 20 |
| 87 | " | " | " | | " | 30 |
| 88 | " | " | " | | " Co salt added | 20 |
| 89 | Small H cell | " | Sat $BeF_2$ | Hg | Sat $BeF_2$ + HCOOH | 1 1/4 |
| 90 | | | | | | 18 |
| 91 | Concentric cell | Large alundum cup | $BeSO_4$ | Hg | $BeSO_4$-HCOOH | 5 |
| 92 | " | | | | | 20 |
| 93 | Concentric cell | " | " | Hg + $CO_2$ | $BeSO_4$ | 5 |
| 94 | " | " | " | " | $BeSO_4$ + $H_2SO_4$ | 15 |
| 95 | 35 mm U cell | Alundum cup | 10% NaOH | Speer graphite | 10% NaOH | 5 |
| 96 | 100 ml beaker | Alundum cup | 10% $H_2SO_4$ | Al. foil | 90% HCOOH | 1 |
| 97 | Concentric cell | Alundum cup | $BeSO_4$ | Hg and $CO_2$ | $BeSO_4$ | 40 |
| 98 | " | | " | Hg | $BeSO_4$ + HCOOH | 3 |
| 99 | " | | | " | " | 20 |
| 100 | " | | | " | Added $BeSO_4$ and HCOOH | 25 |
| 101 | 30 mm U tube | Alundum cup | 10% $H_2SO_4$ | Pd. tube + $CO_2$ | 10% $H_2SO_4$ | 3 |
| 102 | " | | | | | 5 |
| 103 | Steel pressure cell | Alundum cup | 10% $H_2SO_4$ 50 psig $O_2$ | Micrometallic nickel | 10% $H_2SO_4$ 50 psig $CO_2$ | 2 125°F |

| Amps | Cathode Current Density ($ma/cm^2$) | Volts | Tests | Remarks |
|---|---|---|---|---|
| .5 | 33 | 9 | No formate or HCHO | $CO_2$ in |
| .8 | 254 | 18 | Considerable formate | $CO_2$ bubbled through amalgam. |
| .9 | 125 | 18 | No HCHO | |
| " | 125 | " | No HCHO | Ce $(SO_4)_2$ did not appear to dissolve. |
| .2 | 27.8 | 6 | No HCHO | Big deposit of soft grey matter on lead. |
| .2 | 31.8 | 6 | No HCHO | Developed a grey deposit. |
| .4 | 17.8 | 18 | No HCHO | No grey deposit formed. |
| 1.5 | 99 | 18 | No HCHO | $CO_2$ bubbled into Hg. Formed black jelly-like ppt |
| " | " | " | No HCHO | Black ppt. reacted forming a grey ppt. |
| .4 | 128 | 18 | No HCHO | $CO_2$ bubbled into Hg. |
| " | 128 | " | No HCHO | |
| 0.05 | 0.034 | 12 | No HCHO, No $CH_4$ | $CO_2$ bubbled through catholyte |
| 0.29 | 1.99 | 23 | No HCHO, No $CH_4$ | $MgCO_3$ deposit on the cathode |
| 0.05 | 15.9 | 10 | Slightly + Schiff No MeOH | |
| 1.0 | 16.7 | 10 | No HCHO, No HCOOH | $CO_2$ bubbled through catholyte |
| 0.05 | 3.3 | 10 | Much HCOOH | $CO_2$ bubbled through catholyte |
| 0.05 | 3.3 | 10 | Slight HCHO | No $CO_2$ in |
| 2 to 4 | 33.3 - 66.7 | 8 | Slight HCHO | Cell held at about 90°C |
| 3 | 50 | 6 | No additional HCHO | Nothing indicated on gas chromatograph |
| 3 | 50 | 6 | No HCHO | " " |
| 0.035 | 11.3 | 20 | | |
| 0.05 | 16.2 | 26 | No HCHO | |
| 1.0 | 80 | 8 | Good HCHO test | Possible trace MeOH indicated by G.C. |
| 0.2 | 16 | 4 | Good HCHO test | |
| 0.4 | 32 | 10 | No HCHO, some HCOOH | |
| 0.7 | 56 | 10 | No HCHO | Electrolyte ran low |
| 1.1 | 18.3 | 12 | MeOH) HCHO) Neg HCOOH) | White ppt. formed after 4 hrs |
| 0.6 | - | 16 | HCHO-neg | |
| 0.4 | 32 | 10 | HCHO neg | |
| 0.9 | 72 | 10 | Good test HCHO | |
| 0.9 | 72 | 10 | Better test HCHO | |
| 0.9 | | 10 | Not as good HCHO test | No MeOH or HCHO on chromatograph |
| 2.0 | 200 | 10 | Some HCOOH | Became green from corrosion of the support |
| 2.0 | 200 | 9 | HCHO neg $CH_4$ neg | Iron "whiskers" formed on cathode Brown film on Pt anode |
| 1.5 | 231 | 4 | HCHO neg | Produced internal explosions Electrolyte green from corrosion |

| Run | Type of Cell | Diaphragm | Anolyte | Cathode | Catholyte | Time (hrs) |
|---|---|---|---|---|---|---|
| 104 | 2" glass pipe | Alundum cup | Sat BeSO$_4$ 30 psig O$_2$ | Hg | Sat BeSO$_4$ 30 psig CO$_2$ | 3 75°F |
| 105 | " | | 40 psig O$_2$ | | 40 psig CO$_2$ | 2 150°F |
| 106 | " | | " | " | " | 4 210°F |
| 107 | Small U cell | Alundum cup | BeSO$_4$ | Lead rod | BeSO$_4$-HCOOH | 60 |
| 108 | Small H cell | Alundum cup | BeSO$_4$ | Hg-CO$_2$ | BeSO$_4$ | 7 |
| 109 | " | | | | | 20 |
| 110 | Large H cell | Alundum cup | Sat BeSO$_4$ 10% Li$_2$SO$_4$ | Hg-CO$_2$ | BeSO$_4$-Li$_2$SO$_4$ | 7 |
| | Continued | | | | | 80 |
| 111 | Large H cell | " | " | Raney Ni added | " | 34 |
| 112 | 2" glass pipe | Alundum cup | " 40 psig O$_2$ | Hg | " 40 psig CO$_2$ | 20 |
| 113 | " | " | Sat BeSO$_4$ 40 psig O$_2$ | Hg + Raney Ni | BeSO$_4$ 40 psig CO$_2$ | 15 |
| 114 | Small H cell | Small alundum cup | Sat Li$_2$SO$_4$ | Hg + Raney Ni | Li$_2$SO$_4$ + CO$_2$ | 20 |
| 115 | " | " | 10% H$_2$SO$_4$ | " | 10% H$_2$SO$_4$ + CO$_2$ | 20 |
| 116 | " | " | " | " | | 6 |
| 117 | 2" glass pipe | Alundum cup | Sat BeSO$_4$ 40 psig CO$_2$ | Hg + Raney Ni | BeSO$_4$ 40 psig CO$_2$ | 6 |
| 118 | " | " | " | " | " | 6 |
| 119 | " | " | " | " | " | 9 |
| 120 | 30 mm U tube | " | Sat Li$_2$SO$_4$ | Speer carbon + Raney Ni | Li$_2$SO$_4$ + CO$_2$ | 8 |
| 121 | " | " | " | " | Li$_2$SO$_4$ + H$_2$SO$_4$ + CO$_2$ | 8 |
| 122 | Large U cell | Alundum cup | Sat MgSO$_4$ | Lead rod | Sat MgSO$_4$ and 5% HCOOH | 24 |
| 123 | Beaker | Alundum cup | Sat Li$_2$SO$_4$ | Hg | 20% mono-ethanol amine | 1/4 |
| | | | | | " " + CO$_2$ gas | 2 |
| 124 | Beaker | Alundum cup | Sat BeSO$_4$ | Hg | Sat BeSO$_4$ + CO$_2$ | 12 |
| 125 | " | " | " | " | " | 5 |
| | " | " | " | " | " | 27 |
| | | | | | " + HCOOH | 15 |
| 126 | Concentric pressure cell | Alundum cup | Sat BeSO$_4$ | Hg + Raney Ni | Sat BeSO$_4$ 40 psig CO$_2$ | 9 |
| 127 | 2" glass pipe | Alundum cup | Sat BeSO$_4$ + 40 psig O$_2$ | Hg Raney Ni | Sat BeSO$_4$ 40 psig CO$_2$ | 9 |
| 128 | 2" glass pipe | Alundum cup | " | Cd rod Raney Ni | " | 18 1/2 |
| 129 | " | " | " | " | " | 16 |
| 130 | 2" glass pipe | Cation exchange membrane | 10% H$_2$SO$_4$ | Hg | 10% LiCl + CO$_2$ in MeOH | 30 |
| 131 | 2" glass pipe | 2 cation exchange 1 parchment 1 paper cup | 10% H$_2$SO$_4$ | Hg | MgSO$_4$-MeOH + CO$_2$ | 30 |

| Amps | Cathode Current Density $(ma/cm^2)$ | Volts | Tests | Remarks |
|------|-----------------------|-------|-------|---------|
| 0.5 | 15.6 | 20 | HCHO neg | No test made for HCOOH |
| 0.85 | 26.6 | 20 | $CH_4$ neg | $O_2$ in cathode gas. |
| 0.95 | 29.7 | 20 | HCHO neg | 1.4% $CO_2$ in anode gas |
| 0.05 | 2.2 | 12 | HCHO pos | |
| 0.07 | 22.6 | 18 | HCHO neg | No test made for HCOOH |
| 0.09 | 29 | 18 | Trace HCHO | No test made for HCOOH |
| 0.45 | 29.6 | 18 | HCHO neg-HCOOH trace | |
| 0.70 | 46 | 18 | HCHO neg | HCOOH very slight trace. $CH_4$ and $CH_3OH$ neg. |
| 0.70 | 46 | 18 | HCHO neg | |
| 0.5 | 15.6 | 18 | HCHO neg | 2.4% $CO_2$ in anode-$CH_4$ neg |
| 0.5 | 15.6 | 18 | HCHO neg | $CH_3OH$ neg. 0.02% CO or $CH_4$ in cathode gas |
| 0.05 | 16.1 | 20 | | Plugged-blewout electrolyte |
| 0.1 | 32.2 | 6 | HCHO neg | |
| 0.5 | 161 | 8 | HCHO neg | |
| 0.5 | 15.6 | 18 | HCHO neg | |
| 1.5 | 46.8 | 41 | HCHO neg $CH_4$ neg | |
| 2.0 | 62.4 | 42 | HCHO neg MeOH neg $CH_4$ neg | |
| 1.5 | 25 | 20 | HCHO neg | |
| 1.5 | 25 | 20 | HCHO neg MeOH neg $CH_4$ neg | |
| 1.0 | 44.5 | 14 | HCHO neg $CH_4$ neg | |
| 0.02 | 0.74 | 18 | | |
| 2.0 | 74 | 18 | HCHO neg | Preliminary test for conductance, etc. |
| 2.0 | 74 | 10 | HCHO neg | |
| 4.0 | 148 | 18 | HCHO neg | Pulsating D.C. 10 sec. on, 5 sec. off |
| 2.0 | 74 | 10 | HCHO,HCOOH,MeOH,$CH_4$ neg | |
| 0.5 | 18.5 | | HCHO pos | |
| 1-2 | 80 - 160 | 42 | HCHO,HCOOH,MeOH,$CH_4$ neg | Catholyte in center of cell in porous cup heated up |
| 2 | 62.4 | 42 | HCHO,HCOOH,MeOH,$CH_4$ neg | Cell thermostatted at 105°C |
| 2 | 0.89 | 41 | HCHO,HCOOH,MeOH,$CH_4$ neg | |
| 2 | 62.5 | 41 | HCHO,HCOOH,MeOH,$CH_4$ neg | Cell thermostatted at 105°C |
| 0.5 | 15.6 | 8 | Catholyte-HCHO Pos HCOOH Pos Anolyte-$Cl_2$,Cl HCHO Pos, MeOH 2.3% | HCHO possibly came from anodic oxidation of $CH_3OH$ |
| 0.03 | 0.94 | 25 | Catholyte-HCHO Pos, Anode-HCHO Pos, MeOH 5% | " " |

| Run | Type of Cell | Diaphragm | Anolyte | Cathode | Catholyte | Time (hrs) |
|-----|-------------|-----------|---------|---------|-----------|------------|
| 136 | Beaker | Alundum cup | Sat $Na_2SO_4$ | Hg | Sat $Na_2SO_4$ + $CO_2$ | 36 |
| 137 | Beaker | None | Sat $K_2SO_4$ | Hg | Sat $K_2SO_4$ | 34 |
| 138 | Beaker | None | Sat $K_2CO_3$ | Hg | Sat $K_2CO_3$ | 24 |
| 139 | Beaker | Alundum cup | $Li_2SO_4$ | Hg + Hg black | $Li_2SO_4$ + $CO_2$ | 48 |
| 140 | " | " | " | " | " | 20 |
| 141 | Beaker | Alundum cup | 0.1 N KOH | Lead rod | 0.1 N KOH | 73 |
| 142 | " | " | Sat $BeSO_4$ | Pb stick | Sat $BeSO_4$ + $CO_2$ | 41 |
| 143 | Beaker | Alundum cup | $BeSO_4$ + $H_2SO_4$ | Pb stick | $BeSO_4$ + $H_2SO_4$ + $CO_2$ | 48 |
| 144 | " | " | Sat $BeSO_4$ | Pb stick | Sat $BeSO_4$ + $CO_2$ | 36 |
| 145 | " | " | $BeSO_4$ + $H_2SO_4$ | Pb stick | $BeSO_4$ + $H_2SO_4$ + $CO_2$ | 30 |
| 146 | Beaker | Alundum cup | Sat $BeSO_4$ | Zn stick | Sat $BeSO_4$ + $CO_2$ | 41 |
| 147 | " | " | $BeSO_4$ + $H_2SO_4$ | Zn stick | $BeSO_4$ + $H_2SO_4$ + $CO_2$ | 48 |
| 148 | " | " | Sat $BeSO_4$ | Zn stick | Sat $BeSO_4$ + $CO_2$ | 36 |
| 149 | " | " | $BeSO_4$ + $H_2SO_4$ | Zn stick | $BeSO_4$ + $H_2SO_4$ + $CO_2$ | 30 |
| 150 | Beaker | Alundum cup | Sat $BeSO_4$ | Sn stick | Sat $BeSO_4$ + $CO_2$ | 41 |
| 151 | " | " | $BeSO_4$ + $H_2SO_4$ | Sn stick | $BeSO_4$ + $H_2SO_4$ + $CO_2$ | 48 |
| 152 | " | " | Sat $BeSO_4$ | Sn stick | Sat $BeSO_4$ + $CO_2$ | 36 |
| 153 | Beaker | Alundum cup | $BeSO_4$ + $H_2SO_4$ | Sn stick | $BeSO_4$ + $H_2SO_4$ + $CO_2$ | 30 |
| 154 | Beaker | Alundum cup | Sat $BeSO_4$ | Cd stick | Sat $BeSO_4$ + $CO_2$ | 41 |
| 155 | Beaker | Alundum cup | $BeSO_4$ + $H_2SO_4$ | Cd stick | $BeSO_4$ + $H_2SO_4$ + $CO_2$ | 48 |
| 156 | Beaker | Alundum cup | Sat $BeSO_4$ | Cd stick | Sat $BeSO_4$ + $CO_2$ | 36 |
| 157 | Beaker | Alundum cup | $BeSO_4$ + $H_2SO_4$ | Cd stick | $BeSO_4$ + $H_2SO_4$ + $CO_2$ | 30 |

| Amps | Cathode Current Density $(ma/cm^2)$ | Volts | Tests | Remarks |
|------|-----|-----|-------|---------|
| 1 | 141 | 4 | HCHO,MeOH neg HCOOH pos | $CO_2$ bubbled through dry section of cathode. |
| 1.5 | 212 | 5 | HCHO,HCOOH neg | $CO_2$ flow through dry section of Hg cathode |
| 2 | 282 | 7 | HCHO, HCOOH neg | "                                " |
| 2 | 74 | 9 | HCHO, HCOOH, MeOH Neg | |
| 0.5 | 18.5 | 3 | HCHO, HCOOH, MeOH Neg | |
| 0.002 | 0.089 | 3 | HCHO, HCOOH, MeOH Neg | Controlled potential electrolysis |
| 0.6 | 41.4 | 5.2 | HCHO, HCOOH Neg | Pb cathode cast in mold at 25°C |
| 1.6 | 111 | 6.2 | HCHO, HCOOH Neg | Pb cathode cast in mold at 25°C |
| 1.5 | 103 | 8.8 | HCHO, HCOOH Neg | Pb cathode cast in mold at 275°C |
| 1.0 | 69 | 5.0 | HCHO, HCOOH Neg | "                                " |
| 1.3 | 90 | 5.2 | HCHO, HCOOH Neg | Zn cathode cast in mold at 25°C |
| 0.45 | 31 | 6.2 | HCHO, HCOOH Neg | "                                " |
| 0.15 | 10.3 | 8.8 | HCHO, HCOOH Neg | Zn cathode cast in mold at 370°C |
| 1.5 | 103 | 5.0 | HCHO, HCOOH Neg | "                                " |
| 0.44 | 30.3 | 5.2 | HCHO, HCOOH Neg | Sn cathode cast in mold at 25°C |
| 0.55 | 38 | 6.2 | HCHO, HCOOH Neg | "                                " |
| 0.35 | 21.2 | 8.8 | HCHO, HCOOH Neg | Sn cathode cast in mold at 180°C |
| 0.55 | 38 | 5.0 | HCHO, HCOOH Neg | "                                " |
| 1.0 | 69 | 5.4 | HCHO, HCOOH Neg | Cd cathode cast in mold at 25°C |
| 1.15 | 79 | 6.2 | HCHO, HCOOH Neg | "                                " |
| 0.95 | 64.5 | 8.8 | HCHO, HCOOH Neg | Cd cathode cast in mold at 280°C |
| 1.45 | 100 | 5.0 | HCHO, HCOOH Neg | "                                " |

| Run | Type of Cell | Anolyte | Diaphragm | Cathode | Catholyte | Time* (hrs) | Amps. | Cathode Current Density (ma/cm) |
|---|---|---|---|---|---|---|---|---|
| 180 | Battery Jar | Na$_2$SO$_4$ | Porous battery cup | Mercury | Na$_2$SO$_4$ CO$_2$ flow through dry cathode | 3<br>5-1/2<br>15 | 4.0<br>4.0<br>4.0 | 125<br>125<br>125 |
| 181 | Glass "H" Cell | BeSO$_4$ | Alundum cup | Mercury | BeSO$_4$ solution | 11<br>47<br>52 | 1<br>0.1<br>1.2 | 31.3<br>3.1<br>37.5 |
| 182 | Battery Jar | Li$_2$SO$_4$ | Porous battery cup | Mercury | Li$_2$SO$_4$ CO$_2$ flow through dry cathode section | 16<br>23 | 0.1p<br>0.1p | .14<br>14 |
| 183 | Small H-Cell | 5% H$_2$SO$_4$ Sat. K$_2$SO$_4$ | Alundum cup | K amalgam CO$_2$ bubbled through wet K-Hg | K$_2$SO$_4$ | 4-1/2<br>21<br>28<br>49<br>51<br>63 | 0.8<br>0.5<br>0.8<br>0.8<br>1.5<br>0.5 | 257<br>161<br>257<br>257<br>485<br>161 |
| 184 | Large H-Cell | 5% H$_2$SO$_4$ Sat. K$_2$SO$_4$ | Alundum cup | Mercury CO$_2$ bubbled through Hg | K$_2$SO$_4$ | 7<br>23-1/2 | 0.8<br>0.5 | 52.5<br>33 |
| 185 | Steel pressure 50 atms CO$_2$ | Sat. K$_2$SO$_4$ | None | Mercury | Sat. K$_2$SO$_4$ | 4<br>7-1/2 | 1.0<br>1.0 | 114<br>114 |
| 186 | Steel pressure 50 atms CO$_2$ | 1% H$_2$SO$_4$ K$_2$SO$_4$ | None | Mercury | 1% H$_2$SO$_4$ K$_2$SO$_4$ | 3 | 0.5 | 57 |
| 187 | Steel pressure 50 atms CO$_2$ | Sat. K$_2$SO$_4$ | None | Mercury | Sat. K$_2$SO$_4$ | 6 | 0.4 | 46 |
| 188 | 2" Glass pipe | Sat. K$_2$SO$_4$ | Ion exchange membrane (I) | K-Hg CO$_2$ bubbled through K-Hg | Sat. K$_2$SO$_4$ | 4-3/4<br>19-1/4<br>27-1/4<br>49-1/2 | 0.5<br>1.7<br>1.7<br>1.7 | 15.6<br>53<br>53<br>53 |
| 189 | 2" Glass Pipe | Sat. K$_2$SO$_4$ | Ion exchange membrane (I) | K-Hg CO$_2$ bubbled through K-Hg | 5% HCOOH K$_2$SO$_4$ | 2<br>15 | 1.7<br>4.5 | 53<br>140 |
| 190 | Small H-cell | Sat. Li$_2$SO$_4$ | Alundum cup | Mercury CO$_2$ bubbled through Hg | Sat. Li$_2$SO$_4$ + H$_2$SO$_4$ | 2<br>5<br>29<br>109 | 0.2<br>0.15<br>0.2<br>0.2 | 64.5<br>48.5<br>64.5<br>64.5 |
| 191 | Large H-cell | 5% H$_2$SO$_4$ Sat. Li$_2$SO$_4$ | Alundum cup | Mercury CO$_2$ bubbled through Hg | Sat. Li$_2$SO$_4$ | 2<br>11<br>24<br>105 | 2<br>1<br><br>1 | 132<br>66<br><br>66 |
| 192 | Autoclave 50 atms CO$_2$ | Sat. K$_2$SO$_4$ | Alundum cup | Mercury CO$_2$ 50 atms | Sat. K$_2$SO$_4$ | 8 | 1<br>1/2 | 72.8<br>36.4 |
| 192A | Autoclave 50 atms CO$_2$ | Sat. K$_2$SO$_4$ | Mercury | Mercury CO$_2$ 50 atms | Sat. K$_2$SO$_4$ | 3-1/2<br>10-1/2<br>17-1/2<br>23<br>28 | 1.2<br>2.5<br>2.5<br>2.2<br>2.2 | 87<br>182<br>182<br>159<br>159 |
| 193 | Autoclave 50 atms CO$_2$ | Sat. K$_2$SO$_4$ | Alundum cup | Amalgamated zinc | Sat. K$_2$SO$_4$ | 15 | 0.1-1.0 | 0.43-4.3 |
| 194 | Nickel beaker | Sat. Na$_2$SO$_4$ | Alundum cup | Carbon rod | Sat. Na$_2$SO$_4$ | 4-1/2 | 10 | 266 |
| 195 | Beaker | Sat. Na$_2$SO$_4$ | Alundum cup | Carbon rod | Sat. Na$_2$SO$_4$ | 4 | 5-10 | 133-266 |

| Volts | Temperature | Tests | | Remarks |
|---|---|---|---|---|
| | | Gas Phase Products | Catholyte Organic Product | |
| 7 | Ambient | Cathode CH4 neg, CO neg | Negative | Dry section of cathode |
| 7 | Ambient | | Negative | flushed into catholyte |
| 7 | Ambient | | Negative | before each sample. |
| 32 | 30 | Cathode CH4 neg, CO neg | Negative | Recycle mixing of CO2 |
| 9 | 30 | | Negative | at the cathode. Cumulative |
| 45 | 30 | | Negative | gas samples. |
| 3.6 | Ambient | Cathode CH4 neg, CO neg | Negative | Gas collected in dry section |
| 3.6 | Ambient | Cathode CH4 neg, CO neg | Negative | of cathode and flushed into |
| | | | | catholyte before samples. |
| 35 | Water cooled | | HCHO neg, MeOH neg, HCOOH pos. | |
| 28 | Water cooled | | HCHO weak pos, MeOH neg, HCOOH pos. | |
| 35 | Water cooled | | HCHO weak pos, MeOH neg, HCOOH pos. | |
| 35 | Water cooled | | HCHO pos, MeOH neg, HCOOH pos. | |
| | Cathode 70°C | | HCHO weak pos, MeOH neg, HCOOH pos. | |
| 25 | Water cooled | | HCHO pos, MeOH neg, HCOOH pos. | |
| 29 | Water cooled | | HCHO neg, MeOH neg, HCOOH pos. | |
| | Water | | HCHO neg, MeOH neg, HCOOH pos. | |
| 18 | Water cooled | Cathode CH4 neg, CO neg | HCHO weak pos, MeOH neg, HCOOH weak pos. | |
| 18 | Water cooled | Cathode CH4 neg, CO neg | HCHO weak pos, MeOH neg, HCOOH weak pos. | |
| 18 | Water cooled | Cathode CH4 neg, CO neg | HCHO neg, MeOH neg, HCOOH pos. | Electrode blowout |
| 21.5 | Ice bath | Cathode CH4 neg, CO neg | HCHO weak pos, MeOH neg, HCOOH weak pos. | |
| 13 | Water cooled | | HCHO neg, MeOH neg, HCOOH pos. | After 49-1/2 hrs anolyte |
| 13 | | | HCHO neg, MeOH neg, HCOOH pos. | showed weak positive |
| 13 | | | HCHO neg, MeOH neg, HCOOH pos. | test for HCOOH. |
| 13 | | | HCHO neg, MeOH neg, HCOOH pos. | |
| 19 | | | HCHO neg | Electrolyte pushed into |
| 19 | | | | cathode section overnight. |
| 19 | Water cooled | | Negative | 10 cc 10% H2SO4 added to |
| 19 | | | HCHO neg, MeOH neg, HCOOH weak pos. | catholyte after 5 hrs. |
| 19 | | | HCHO neg, HCOOH pos. | |
| 19 | | | HCHO neg, MeOH neg, HCOOH pos. | |
| 24 | Water cooled | | Negative | |
| 24 | | | | |
| | | | HCHO neg, MeOH neg, HCOOH pos. | |
| 24 | | | HCHO neg, MeOH neg, HCOOH neg | |
| 5.2 | Water cooled | CH4 and CO neg. | HCHO neg, MeOH neg, HCOOH weak pos. | Cathode contact wire pushed out of Hg by pressure sometime after 5 hrs. |
| 4.5 | Water cooled | CH4 and CO neg. | HCHO neg, MeOH neg, HCOOH weak pos. | |
| 5.5 | Water cooled | CH4 and CO neg. | HCHO neg, MeOH neg, HCOOH weak pos. | |
| 5.5 | | 0.04% CO | | |
| 5.7 | | 0.04% CO | | |
| 6.0 | | 0.04% CO | HCHO neg, MeOH neg, HCOOH pos. | |
| | Water cooled | | HCHO neg, MeOH neg, HCOOH pos. | Cathode broke off. 0.1 amp on overnight to counter galvanic effect. Next morning cell was warm and 1 amp current. |
| 6.5 | Oil cooled | 0.04% CO | HCHO neg, MeOH neg, HCOOH neg. | Cathode gas collected in gas buret. |
| 6-7 | Oil cooled | 0.07% CO | HCHO neg, MeOH neg, HCOOH neg. | Cathode gas collected in gas buret. |

| Run | Type of Cell | Anolyte | Diaphragm | Cathode | Catholyte | Time (hrs) | Amps | Cathode Current Density (ma/cm) |
|---|---|---|---|---|---|---|---|---|
| 196 | Beaker | Sat. $K_2SO_4$ | Alundum cup | 1 in. diameter carbon impregnated with Hg | Sat. $K_2SO_4$ | 7<br>11-1/2 | 1<br>1 | 26.6<br>26.6 |
| 197 | 2" Glass pipe | Sat. $K_2SO_4$ | Ion exchange membrane (N) heavy | Hg | Sat. $K_2SO_4$ | 3<br>16<br>28 | 1.0<br>.35<br>.35 | 31.2<br>10.9<br>10.9 |
| 198 | Battery jar | Sat. $K_2SO_4$ | Alundum cup | Cd Fe mix 3 x 6" plate | Sat. $K_2SO_4$ | 5<br>26-1/2<br>46-1/2 | 1.4<br>1.4<br>1.4 | 6.3<br>6.3<br>6.3 |
| 199 | Large H-cell | Sat. $K_2SO_4$ | Alundum cup | Cd powder on Ag grid | Sat. $K_2SO_4$ | 7-1/2 | 0.8 | 61.8 |
| 200 | Battery jar | Sat. $K_2SO_4$ | Alundum cup | Cd Fe mix 3 x 6" plate amalgamated | Sat. $K_2SO_4$ | 32 | 1.5 | 6.75 |
| 201 | Large H-cell | Sat. $K_2SO_4$ | Alundum cup | Cd powder on Ag grid amalgamation | Sat. $K_2SO_4$ | 32 | 0.5 | 38.5 |
| 202 | Autoclave 50 atms $CO_2$ | Sat. $K_2SO_4$ | Alundum cup | Amalgamated Zn | Sat. $K_2SO_4$ | 2-1/2<br>17-1/2<br>24 | 1.5<br>0.1<br>1 | 6.45<br>0.43<br>4.3 |
| 203 | Autoclave 50 atms $CO_2$ | Sat. $K_2SO_4$ | Alundum cup | Amalgamated Cu | Sat. $K_2SO_4$ | 3<br>6<br>14 | 1<br>1<br>1 | 4.3<br>4.3<br>4.3 |
| 204 | Beaker | Sat. $K_2SO_4$ | Alundum cup | Hg | Sat. $K_2SO_4$ | 92 | 25 | 2000 |
| 205 | 2" Glass pipe | Sat. $K_2SO_4$ | Alundum cup | Hg | Sat. $K_2SO_4$ 20 gm $Ce(SO_4)_2 \cdot$ 10 $H_2O$ per liter | 100 | 1 | 31.2 |
| 206 | 2" Glass pipe | Sat. $K_2SO_4$ | Alundum cup | Hg | Sat. $K_2SO_4$ 10 gm cobaltic acetate per liter | 100 | 1 | 31.2 |

\*  Cumulative time
I  Ionac MC 3142 cation exchange membrane
p  Pulsating current, 10 seconds on, 5 seconds off
N  Nepton CR-61 cation exchange membrane

| Volts | Temperature | Gas Phase Products | Tests Catholyte Organic Product | Remarks |
|-------|-------------|--------------------|---------------------------------|---------|
| 3.4 | Ambient | Cathode CH$_4$ & CO neg. | HCHO neg, MeOH neg, HCOOH neg. | |
| 3.5 | Ambient | Cathode CH$_4$ & CO neg. | HCHO neg, MeOH neg, HCOOH neg. | |
| 15 | Oil cooled | | Negative | Osmosed into catholyte (about 1/2 of anolyte) |
| 6 | | | Negative | |
| 6 | | | Negative | |
| 6.2 | Water Cooled | | Negative | |
| 6.2 | | | Negative | |
| 6.2 | | | Negative | |
| 13 | Oil cooled | | Negative | |
| 6.2 | Water cooled | | Negative | |
| 7.0 | Oil cooled | | Negative | |
| 4.6 | Water cooled | | Negative | |
| 3.1 | | 0.07% CO | | |
| 4.1 | | 0.02% CO | Negative | |
| 4.1 | Water cooled | 0.04% CO | | HCOOH pos. anolyte and catholyte |
| 4.1 | | 0.03% CO | | |
| 4.1 | | Trace CO | | |
| 5.3 | Water cooled | | HCHO neg, HCOOH pos. | |
| 14.8 | Water cooled | | HCHO neg, HCOOH weak pos. | |
| 12.0 | Water cooled | | HCHO neg, HCOOH weak pos. | |

TABLE 3 - CATHOLYTE SOLUTIONS WITH EXTREMELY POOR CONDUCTIVITY
AT 45-48 VOLTS

*Concentrations ? & values*

| Ether Solvent | Bis-2-dimethoxyethyl Ether Solvent | Anisole Solvent |
|---|---|---|
| $Li_2SO_4$ | $Li_2SO_4$ | $LiCl$ |
| $K_2SO_4$ | $LiCl$ | $Li_2SO_4$ |
| $LiCl$ | $NaNO_3$ | $NaCl$ |
| $BeSO_4$ | $Na_2CO_3$ | $Na_2SO_4$ |
| | $BeCl_2$ | $MgSO_4$ |
| | $K_2CO_3$ | |
| | $MgSO_4$ | |

TABLE 4 - ORGANIC SYSTEMS WITH CONDUCTIVITY
BUT NO SIGNIFICANT REDUCTIONS

*Concentrations - values.*

$LiCl$ in acetone

$LiCl$ in pentanone

$LiCl$ in pyridine (with and without Raney nickel catalyst)

$LiCl$ in acetonitrile (with and without Raney nickel catalyst)

$LiCl$ in propylene carbonate

The source of direct current used in these experiments was rectified alternating current up to 110 volts. The higher voltages were used for the non-aqueous systems. Several experiments were performed with pulsating d.c. 10 seconds on and five seconds off. A proportional timer in series with a relay provided a reliable automatic pulsating current.

## a. Cathode Material and Structure

Table 5 lists the various materials used as cathodes in exploratory studies. Emphasis was placed on materials with high hydrogen overvoltages; but a few other materials were tried for

TABLE 5 - MATERIALS SCREENED AS POSSIBLE CATHODES

| High Overvoltages | Large Surface Areas | Reducing Agents |
|---|---|---|
| Pb, Cd, Hg, Zn, Zn-Hg, Cu-Hg, Sn, Mg, Pb | C, porous Ni | K-Hg, Mg |
| | Other | |
| | Pd, Al | |

reasons of having large surface areas, of being permeable to hydrogen or of being reducing agents. Hydrogen overvoltages are related to position of the cathode metal in the Periodic Table[22] as is shown in Table 6. It is seen that Group II metals have high typical overvoltages; and thus, cadmium, mercury and its amalgams, zinc and magnesium were chosen for high hydrogen overvoltages; carbon and porous nickel for high surface areas; palladium for its permeability to hydrogen and catalytic properties; and platinum also for its catalytic properties. Lead has an anomously high overvoltage at high current densities considering its position in the Periodic Table and was thus tested also.

TABLE 6 - HYDROGEN OVERVOLTAGE OF METALS AND THEIR
POSITION IN THE PERIODIC TABLE

| Group in the Periodic Table | Metal | Typical Overvoltage |
|---|---|---|
| I | Na, Cu, Ag, Au | 0.35 volt |
| II | Mg, Zn, Cd, Hg | 0.70 volt |
| III | Al, Tl | 0.50 volt |
| IV | C, Sn, Pb | 0.45 volt |
| V | Sb, Ta, Bi | 0.42 volt |
| VI | Cr, Mo, W | 0.32 volt |
| VII | Mn | 0.25 volt |
| VIII | Fe, Ni, Rh, Pt, Ir | 0.18 volt |

Since physical condition of the cathode often influences its reducing ability and since casting temperature can influence the physical state of metals, tests were made on the effect of casting temperature upon cathode performance. Table 7 shows materials and temperatures used in the tests.

TABLE 7 - CASTING TEMPERATURES OF VARIOUS CATHODE MATERIALS

| Material | Pb | Zn | Sn | Cd |
|---|---|---|---|---|
| Casting Temp. (°C) | 25, 275 | 25, 370 | 25, 180 | 25, 280 |

Because of the varied experiments and type cells studied it was not feasible to use a standard electrode area and shape. The cathodes were generally used in the form obtained such as solid round or rectangular bars, sheets, screen or liquid mercury and amalgams. The cathode shapes and dimensions were dictated by the type of cell. Simple glass cells such as the "H" or "beaker" type required only that the cathode material extended above the electrolyte so that the connecting wires would be clear of the electrolyte. Special electrodes were required for the high pressure cells. The solid electrodes were attached to a stainless steel rod which served as the connecting lead through an insulated Conax electrode gland. Cathodes in sheets form such as lead, zinc and copper were placed by the same method. The cathode material was attached to the 1/8 in. stainless steel rod above the electrolyte level. The section of the stainless steel rod that was exposed inside the cell was wrapped with Teflon tape in order to protect against corrosion products contaminating the electrolyte. Mercury cathodes were usually placed inside small glass or plastic cups in the cathode area of the cell. Contact was made by platinum wire sealed in a glass tube. For pressure cells this type of contact was soldered to a 1/8 in. rod which served as the connecting lead through a Conax electrode gland.

Under conditions of the tests, reduction of $CO_2$ was obtained only with mercury or certain amalgams (K-Hg and Zn-Hg) as cathodes and to a limited extent with palladium. The tests were carried out in different manners, depending upon the nature of the cathode. In the case of a liquid cathode, $CO_2$ was bubbled through the liquid metal and into the catholyte during electrolyte or through the liquid metal and into the air (Fig 1). In the case of exhausting

CO₂ IN →

¼" GLASS TUBE

ST ³⁴/₄₅

CATHODE CONNECTOR

GLASS INSULATOR

VENT →

PRESSURE REGULATOR

MERCURY

ANODE
PLATINUM WIRE

+

−

ELECTROLYTE

POROUS CUP

MERCURY
CATHODE
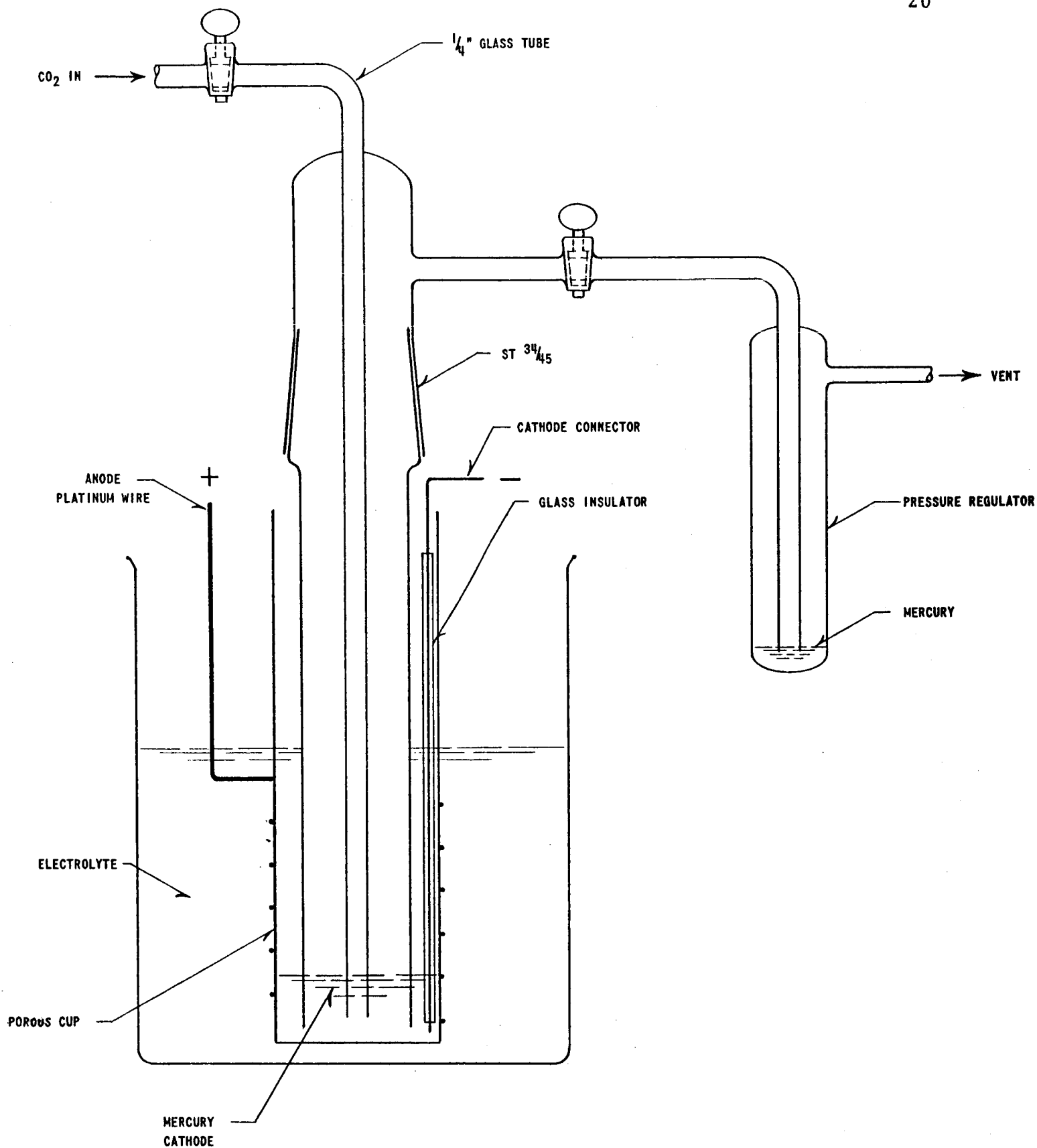
R-1477

FIG 1 - DRY AMALGAM CELL

to the air, the reduction products were exposed to hydrolysis action
from time to time to repeat the conditions of Miller et al[12], who
exposed the reaction products to hydrolysis by the action of
$3NH_2SO_4$. Alternately, an attempt was made to hydrolyze reaction
products on a closed cycle basis. This was accomplished by shutting
off the vent and forcing the dry liquid amalgam under $CO_2$ pressure
into the electrolyte solution. In the case of porous materials,
the gas was forced out of the pores and into the electrolyte; and
in case of solid cathodes contact was only by dissolved $CO_2$, at
times under pressure. Coulombic efficiencies of as high as about
20% were measured with a mercury cathode and about 12% with amalga-
mated copper using $K_2SO_4$ electrolytes.

b. Diaphragms

        Diaphragms can serve to prevent transfer of oxidizable cathode
products to the anode compartment where they might be oxidized or
to prevent mixing of anolyte and catholyte. In the latter case, ion-
exchange membranes were considered useful, especially where it was
desirable to keep aqueous anolytes from contaminating anhydrous
organic catholytes. Cation exchange membranes thus would permit
transport of current by means of transfer of hydrogen ions from
anolyte to catholyte. Table 8 lists the types of diaphragms used.

TABLE 8 - TYPES OF DIAPHRAGMS USED

| | |
|---|---|
| Porous alundum | Parchment |
| Porous alundum plus cellophane | Nepton CR-61 Cation-exchange membrane |
| Cellophane | Ionac MC-3142 Cation-exchange membrane |

        No effects of use of membranes in reduction of $CO_2$ were shown,
possibly because of the low concentrations of formic acid produced.
In the case of starting with high concentrations of formic acid
in the catholyte to determine its reducibility, electrical endos-
mosis of anolyte into catholyte occurred, through the cation ex-
change membranes, interfering with cell operation. Furthermore,
it was found that the ion-exchange membranes had a finite per-
meability to water, water content of the catholyte did build up
to as high as 20%.

### c. Catalysts and Promoters

Exploratory tests on use of potential reduction promoters and catalysts failed to show promise. These materials were either suspended in the catholyte or dissolved therein, depending on whether they were insoluble or soluble. A list of materials tested is given in Table 9.

TABLE 9 - MATERIALS TESTED FOR PROMOTER AND CATALYST ACTIVITY

| | | |
|---|---|---|
| Raney Nickel | $Ce(SO_4)_2$ | $Co(CH_3COO)_2 \cdot 4H_2O$ |
| Mercury Black | $Sb_2O_5$ | |

### d. Catholytes

As will be pointed out in Collation with the Literature below, strongly acid electrolytes and electrolytes of the sulfates of potassium, sodium and lithium have been reported as promoting reductions. Such solutions were tested in studies of electrolyte composition. Similar salts were also tested, especially those with high decomposition potentials. These included the sulfates of beryllium and magnesium.

In efforts to increase the discharge potential of the electrolyte by reducing hydrogen ion concentration in the catholyte, organic catholyte solvents were tested in combination with cation exchange membranes and aqueous anolytes to provide anodic oxygen. The organic catholytes were prepared by placing the catholyte salt to be used in a 500 ml flask and adding the organic solvent. The mixture was stirred several hours to insure saturation. The prepared catholyte was then transferred to the cathode compartment of the cell along with some solid electrolyte to insure maximum saturation. The cell arrangement for this is shown in Fig 2. The literature shows deposition of beryllium from ethereal solutions and of lithium from acetone[10,16] and pyridine[13] and these systems were tested along with other similar ones as indicated in Table 10, which also shows the complete list of catholyte systems tested. The cell incorporates pressure balance controls to prevent mixing of cathode and anode gases and to prevent pressure unbalances that might rupture the membrane. Control involves use of two
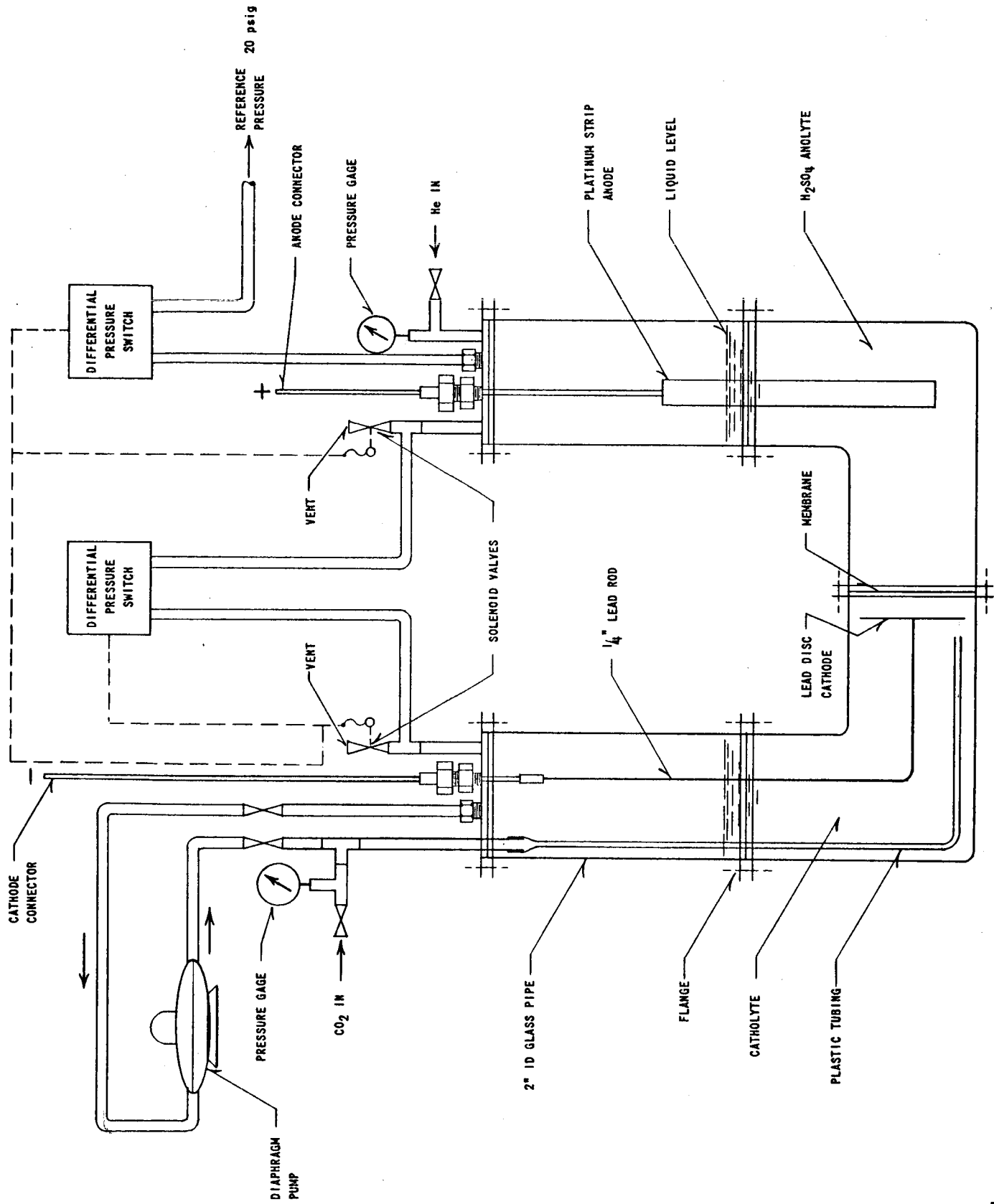
FIG 2 - GLASS PIPE PRESSURE CELL

R-1454

## TABLE 10 - CATHOLYTE SYSTEMS TESTED

| Aqueous | Non-Aqueous |
|---|---|
| $Li_2SO_4$ | monoethanol amine |
| $Li_2SO_4 + H_2SO_4$ | $MgSO_4$ in methanol |
| $Na_2SO_4$ | $BeSO_4$ in dioxane |
| $Na_2SO_4 + H_2SO_4$ | $K_2SO_4$ in dioxane |
| $K_2SO_4$ | $Li_2SO_4$ in dioxane |
| $K_2SO_4 + H_2SO_4$ | $Li_2SO_4$, $K_2SO_4$, LiCl, $BeSO_4$, $MgSO_4$ in diethyl ether |
| $MgSO_4$ | $Li_2SO_4$, LiCl, $NaNO_3$, $Na_2CO_3$, $BeCl_2$, $K_2CO_3$ in bis-2-dimethoxyethyl ether |
| $BeSO_4$ | |
| $H_2SO_4$ | LiCl in acetone, pentanone, pyridine, acetonitrile, propylene carbonate |
| KOH | |
| $BeF_2$ | LiCl, $Li_2SO_4$, NaCl, $Na_2SO_4$, $MgSO_4$ in anisole |

differential switches and two solenoid valves. One switch, operating through a relay, controlled venting of the cathode and anode gases according to a set reference pressure. The other switch controlled the cathode vent according to the pressure differential between the anode and cathode. In this way the cathode, which evolves hydrogen at twice the rate of oxygen at the anode, would vent and maintain equal pressures. Excessive increase of cell pressure over reference pressure is relieved through the other switch on the anode. Relief of cathode pressure would occur simultaneously by operation of the first switch.

The organic systems, with the exception of that with methanol as solvent, all had high resistivity so that any reduction if any would be accomplished with low energy efficiency; and none excepting possibly methanol gave indications of reduction. With use of mercury cathodes, the following aqueous catholytes gave reduction of $CO_2$ to formic acid: $Li_2SO_4$, $K_2SO_4$, $Na_2SO_4$ and $BeSO_4$. These same systems gave reduction of some formic acid to small amounts of formaldehyde when high concentrations of formic acid were built up prior to electrolysis. Any electrochemical reactivity in methanol may have been that of the anodic oxidation of methanol rather than cathodic reduction of $CO_2$. This is because while membranes were used to inhibit transfer of methanol to the anolyte, this inhibition was not very effective and methanol was detected in the anolyte at the end of the runs.

e.  Pressure

Several types of pressure tests were run up to 50 psig. One of them was in a glass cell made by joining two standard flanged glass pipe ells with a 4 in. flanged nipple on each side.(Fig 2) Closure was accomplished by flanging special plates to the tops of the two legs of the cell. Provision was made to permit sampling both anode and cathode compartments, which were separated by use of membranes at the connecting flange.

Another type of pressure run at 50 psig was made in a 4 in. glass pipe cup having a concentric cathode compartment and platinum-rhodium unimesh anode. The cathode was a pool of mercury in a container at the bottom of an alundum cup (Fig 3).

In order to develop higher pressures of $CO_2$ for reduction, two other types of cell were used. One consisted of a steel pipe lined with a polyethylene cup having a mercury cathode of 8.8 $cm^2$ area at the bottom. Cathode connection was made with a Teflon-insulated platinum-tipped wire fitted through a Conax electrode gland. Pressures up to 50 atmospheres were developed in these tests.
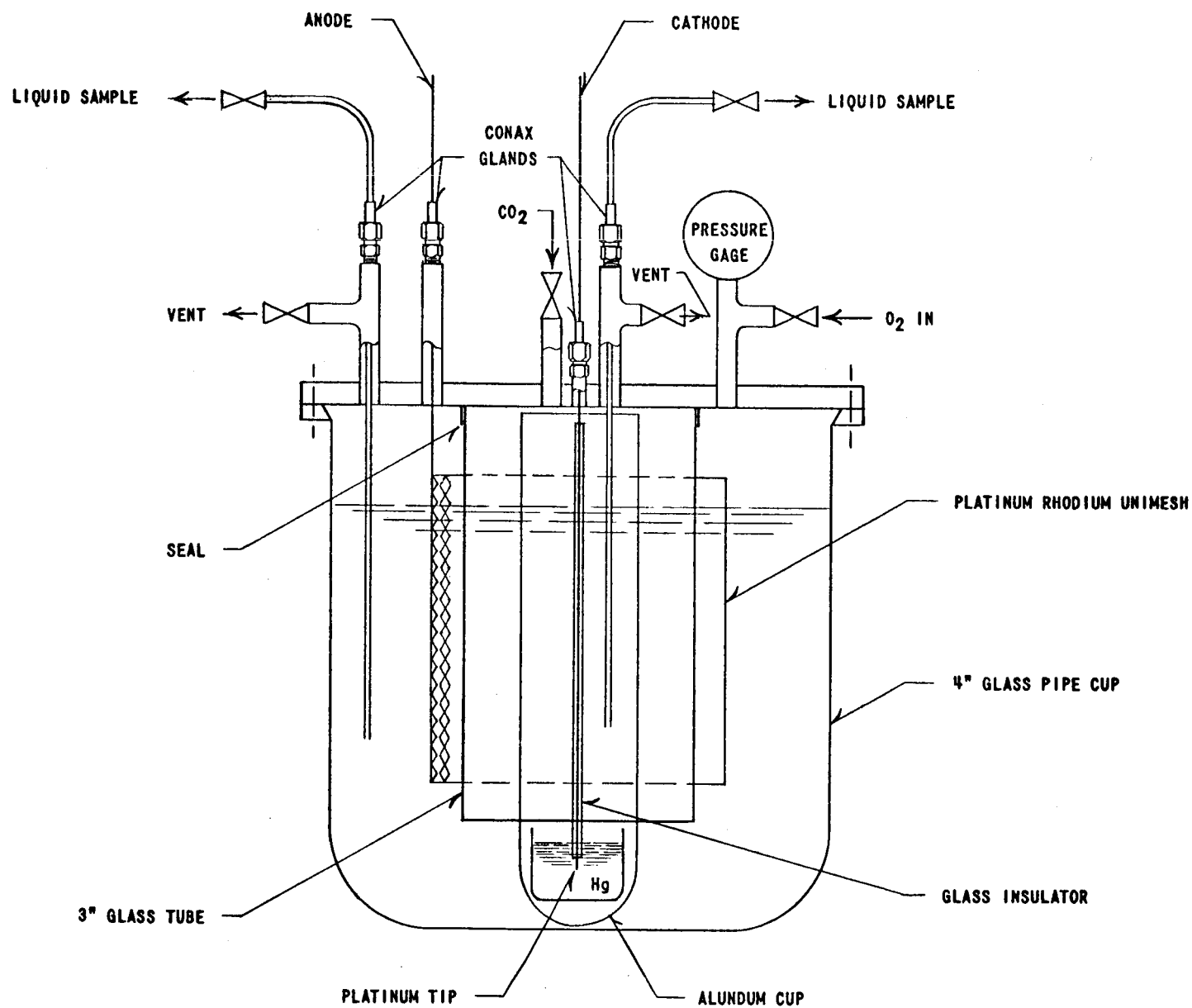
R-1386

FIG 3 - CONCENTRIC PRESSURE CELL

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Another type of high pressure run was made in a one liter autoclave equipped with a stirrer to provide agitation of the electrolyte during electrolysis. The gas phases from the anode and cathode were mixed in the autoclave; and analysis did not distinguish between the two product streams.

No beneficial effects of increased pressure were observed in any of the runs.

## f. Temperature

It was necessary to provide some means of temperature control for the cells during extended tests in order to minimize localized heating at the electrode areas. The cells were placed in cooling baths of running tap water that maintained temperatures of 25-30°C. Cooling for low temperature tests was done by placing the cell in an ice bath. Cold mercury cathodes were obtained in several tests by submerging dry ice in the mercury cathode. This served a dual purpose in that the dry ice supplied the $CO_2$ at the cathode. Thermostatted oil baths were used for uniform elevated temperature operation.

Runs 53, 56, 58, 60, 61 and 169 were made with the cells held at lowered temperature and runs 86, 103-106, 117-119 and 127-129 at elevated temperatures to see if significant improvement in reduction might be thereby obtained. No such improvement was observed.

## g. Summary on Reduction of Formic Acid

Since formic acid is an intermediate in the reduction of carbon dioxide to formaldehyde, some runs were made to determine reducibility of formic acid to formaldehyde directly. Success was attained in runs 1, 3, 16, 22, 25-31, 36-39, 44-45, 48-50, 52, 85-86, 91-92, 99-100, 107, 109, 125 and 130-131. There is some evidence that in the earlier runs (1-52) reduction was chemical since the zinc and magnesium cathodes showed signs of corrosion in areas remote from the anodes and since zinc metal was seen to be redeposited in areas near the anode. Furthermore, the reductions were obtained only at low current densities, at which only poor cathodic protection against corrosion is obtained.

All other strongly positive tests were obtained with mercury cathodes and $BeSO_4$ catholytes. No exceptions were found on reducibility of formic acid with this system, which may be based on the fact that the very active beryllium metal does not amalgamate with mercury.[25]

## h.  Summary on Reduction of Carbon Dioxide

Reduction of carbon dioxide to formic acid was regularly accomplished with mercury cathodes and sulfates of alkali metals as electrolytes in glass cells at room temperature.  Current densities ranged from $0.4$ ma/cm$^2$ to 485 ma/cm$^2$; and a coulombic efficiency (run 184) as high as 20% was measured.  Runs 58, 63, 183-5, 187, 188, 190, 191, 192A and 204 form the basis of this generalization.

Non-reproducible reductions were obtained with a similar cathode and BeSO$_4$ electrolyte (runs 84 and 93) and with similar electrolytes with zinc and mercury amalgam cathodes (run 193 and 203).  Some reduction was also observed with sulfuric acid electrolyte and a palladium cathode (run 101).

Reductions of carbon dioxide beyond formic acid were only in trace amounts at best.

## V.  COLLATION WITH THE LITERATURE

A basic reference to reduction of $CO_2$[3] indicates that pure aqueous solutions and strongly acid solutions of carbon dioxide yield traces of formic acid, that there is good reduction with cathodes of mercury, amalgamated zinc, zinc or amalgamated copper.  Lead cathodes were reported to work well under certain conditions; and electrolytic zinc, amalgamated copper and specially prepared lead cathodes are to give good results.[19]  Increased pressures were reported to promote reduction and solutions of the sulfates of potassium, sodium or lithium to be the best electrolytes.[10]

We have observed reduction of $CO_2$ to formic acid consistently with mercury cathodes and catholytes of lithium sulfate, potassium sulfate or beryllium sulfate; and concentrations of formic acid between one and two percent have been built up.  However, coulombic efficiencies have proved to be very low as is shown in Table 11; and concentrations of formic acid built up from $CO_2$ have not proved large enough to permit further reduction to formaldehyde or methanol. Energy efficiencies were even lower with operating voltages running many times the normal decomposition voltages of alkali metal salts. In the case of run 203, with an operating voltage of 4.1 volts, compared with a reversible voltage of 1.02, energy efficiency was found to be about 3%.

Tafel[18] supports the use of cathodes with high hydrogen over-voltages such as lead and mercury for reduction of compounds reducible only with difficulty, and other metals such as those in Group II of the Periodic Table.  Mg, Zn and Cd fall into this category.  This is because the higher the hydrogen overpotential of the electrode generally the more powerful is its reducing ability, or the greater the energy content of the hydrogen liberated.  This overpotential is simply difference between the potential at which gas evolution is first observed and the theoretical reversible potential of the electrode in the same solution.  We have made exploratory studies of these metals and have found only mercury to give consistently positive results under conditions of the tests.  Similarly we have made tests on the effect of working of the metals, described as sometimes critical[13]; and under conditions of the tests were not able to observe any effect.  Higher overvoltages are reported[19] to be obtained at higher current densities and at lower temperatures; but here again under conditions of our tests, no effects were observed.  Carbon is listed[5] as

TABLE 11 - SUMMARY OF EXPERIMENTAL CONDITIONS INVOLVING QUANTITATIVE ANALYSES

| Run No. | $CO_2$ Pressure Atmos. | Cathode | Catholyte | Anolyte | Current Density $a/cm^2$ | HCOOH Content $g/cc \times 10^3$ | Coulombic Efficiency (%) |
|---|---|---|---|---|---|---|---|
| 183 | 1 | Hg-K | $K_2SO_4$ | 5% $H_2SO_4$ in sat. $K_2SO_4$ | 0.25-0.16 | 7.36 | 0.8 |
| 184 | 1 | Hg | $K_2SO_4$ | 5% $H_2SO_4$ in sat. $K_2SO_4$ | 0.03-0.05 | 11.08 | 19.8 |
| 190 | 1 | Hg | $Li_2SO_4$ | $Li_2SO_4$ | 0.06 | 5.55 | 1.6 |
| 191 | 1 | Hg | $Li_2SO_4$ | 5% $H_2SO_4$ in sat. $Li_2SO_4$ | 0.06 | 2.02 | 1.0 |
| 192 | 50 | Hg | $K_2SO_4$ | $K_2SO_4$ | 0.07 | 1.32 | 0.16 |
| 202 | 50 | Hg-Zn | $K_2SO_4$ | $K_2SO_4$ | 0.0004 to 0.006 | 0 | 0 |
| 203 | 50 | Hg-Cu | $K_2SO_4$ | $K_2SO_4$ | 0.0043 | 7.12 | 11.7 |

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having a fairly high hydrogen overvoltage; and use of this material
has been suggested[7] for the synthesis of alcohols. No reduction
of $CO_2$ was observed in our tests; but a slight amount of formalde-
hyde was obtained from reduction starting with formic acid.

Salts of Cu, Ti, Sn, Pb and V and the oxides of As and Sb
have been reported[17] to be promoters of reduction; but here again
under conditions of our tests no effects were observed.

Reductions of formic acid to formaldehyde were found under a
variety of conditions when starting with high concentrations of
formic acid; but apparently the concentrations of HCOOH developed
in reduction of $CO_2$ are not high enough to yield formaldehyde from
$CO_2$. $BeSO_4$ electrolyte with cathodes of Hg or Pb gave the best
tests. No yields of methanol or methane have been obtained even
though they have been reported in the literature.[8,1] As opposed
to the references on good reduction, it should be pointed out that
there is precedent in the literature for our difficulty in re-
ducing formic acid[2] and for failure to reduce $CO_2$ beyond formic
acid.[4,9] Even when direct chemical reductions with magnesium were
performed, yields of formaldehyde were reported as very small.[9]

If the concentration of organic product can be built up in
further development, separation of such compounds should be studied.
Single stage distillation would not effect separation.[15] Adsorption
on a fixed or moving bed of activated charcoal should be given
consideration on the basis of favorable citation of such pro-
cesses.[21,14]

## VI. CONCLUSIONS

It has been demonstrated that carbon dioxide might be re-
duced to formic acid in concentrations up to 1 or 2 per cent and
with coulombic efficiencies up to 20 per cent and measured energy
efficiency of about 3 per cent in the case of run 203. Reduction
to formaldehyde has been regularly accomplished with mercury
cathodes and beryllium sulfate anolytes but only with higher con-
centrations of formic acid and not directly from carbon dioxide.
Since competitive systems operate at higher energy efficiencies
and since a workable system for control of cabin atmospheres by
cathodic reduction requires production of at least 50% formalde-
hyde, further work on this system was not deemed feasible.

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